

## UNIVERSITI MALAYSIA PAHANG

### BORANG PENGESAHAN STATUS TESIS♦

**JUDUL : PRODUCTION OF BIODIESEL FROM CASTOR OIL USING  
EGG SHELL WASTE AS SOLID CATALYST**

**SESI PENGAJIAN : 2011/2012**

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PRODUCTION OF BIODIESEL FROM CASTOR OIL USING EGG SHELL WASTE  
AS SOLID CATALYSTS

NUR FARZANA BINTI OMAR

Report submitted in partial fulfilment of the requirements for the award of the degree of  
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering  
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JUNE 2012

### **SUPERVISOR'S DECLARATION**

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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### **STUDENT'S DECLARATION**

I hereby declare that this thesis entitled “Production of Biodiesel from Castor Oil using Egg Shell Waste as Solid Catalyst is the result of my own research except for quotations and summaries which have been cited in references. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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**DEDICATION**

*Special dedication to my beloved parents; Mak and Abah,  
My lovely siblings,  
Thank you for your unlimited support.*

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I must also acknowledge to all Chemical & Natural Resources Engineering Laboratory Staffs for all their help, suggestions and technical assistance throughout my research.

Not to forget, a very special thank you to my lovely friend Safiah, Syikin, Sufinah and Raihanah for always being so helpful and friendly. I also thank my friend (too many to list but you know who you are) for providing friendship and support that I needed. For my only one, you are my first supporter. Thank you.

Last but not least, sincerely thank you to my parents; Mak and Abah, my brothers and sister for their support; both emotionally and financially, love and sacrifice throughout my life.

## **ABSTRACT**

The increase in price of petroleum and environmental concerns, the search for alternative fuels has gained importance. Biodiesel is one of several alternative fuels that is renewable and can be manufactured from vegetable oils. Biodiesel's physical properties are similar to those of petroleum diesel, but it is a cleaner-burning alternative. Using biodiesel in place of petroleum diesel can reduce emissions. The main objectives of the research is to produce biodiesel from castor oil using activated egg shell waste as solid catalysts and to investigate the effect of methanol/oil ratio, temperature and reaction time on the biodiesel yield. The effect of parameters on the biodiesel yield has been investigated from the reaction process that is called transterification process. Biodiesel has been successfully produced from castor oil using activated egg shell waste as solid catalyst by the variation of methanol/oil ratio, temperature and reaction time has affected the biodiesel yield. The highest biodiesel yield was found by the methanol/oil ratio of 5:1, temperature of 55°C and reaction time of 4 hours.

## ABSTRAK

Disebabkan oleh kenaikan harga minyak mentah dan kebimbangan terhadap alam sekitar, penyelidikan terhadap bahan bakar alternatif telah menjadi lebih penting. Biodiesel adalah salah satu daripada beberapa bahan bakar alternatif yang boleh diperbaharui dan boleh diperbuat daripada minyak sayuran. Sifat fizikal biodiesel adalah sama dengan minyak mentah, tetapi ia adalah alternatif pembakaran yang lebih bersih. Menggunakan biodiesel di tempat minyak mentah boleh mengurangkan pencemaran udara. Objektif utama penyelidikan ini adalah untuk menghasilkan biodiesel daripada minyak kastor menggunakan sisa cangkerang telur yang diaktifkan sebagai pemangkin dan untuk mengkaji kesan nisbah metanol / minyak, suhu dan masa reaksi pada hasil biodiesel. Kesan parameter pada hasil biodiesel diperolehi dari proses tindak balas yang dipanggil proses transester. Biodiesel telah berjaya dihasilkan daripada minyak kastor menggunakan sisa cangkerang telur diaktifkan sebagai pemangkin pepejal oleh variasi nisbah metanol/minyak, suhu dan masa tindak balas telah dapat menghasilkan biodiesel. Hasil biodiesel tertinggi didapati oleh nisbah metanol/minyak pada 5:1, suhu pada 55°C dan reaksi masa selama 4 jam.



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**LIST OF SYMBOLS**

%	Percent
°C	Degree Celsius
°F	Degree Fahrenheit
g	Gram
h	Hour
mL	Milliliter
μL	Microliter
μm	Micrometer
Wt %	Weight percent

**LIST OF ABBREVIATIONS**

BaO	Barium Oxide
CaCO <sub>3</sub>	Calcium Carbonate
CaO	Calcium Oxide
FAME	Fatty acid methyl esters
GC-MS	Gas chromatography–mass spectrometry
H <sub>2</sub> SO <sub>4</sub>	Sulphuric Acid
HCl	Hydrochloric Acid
K <sub>2</sub> CO <sub>3</sub>	Potassium Carbonate
KOH	Potassium Hydroxide
MeOH	Methanol
MgO	Magnesium Oxide
Na <sub>2</sub> CO <sub>3</sub>	Sodium Carbonate
NaOH	Sodium Hydroxide
SrO	Strontium Oxide
ZnO	Zinc Oxide

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 RESEARCH BACKGROUND**

Recent concerns over the environment, increasing fuel prices, and scarcity of supply have promoted interest in the development of alternative source to petroleum fuels. Due to the global prices of fuel are going up day after day, biodiesel extracted from vegetable oil is one such renewable alternative under consideration. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. Biodiesel has been defined as a mono-alkyl ester of vegetable oil or animal fats (Knothe, 2005). These resources can be re-grown and considered infinite in comparison to crude oil that is limited. When using biodiesel instead of petrodiesel, the demand for crude oil products is reduced and as a result their prices decrease. There are many types of vegetable oil such as castor oil, jatropha oil, and soybean oil. Biodiesel is produced through a refinery process called transesterification reaction of vegetable oils and animal fat. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production.

Many researchers use edible oils such as soybean oil and corn oil to produce biodiesel. The price of edible oils keeps increasing due to demand for nutritional need. In order to overcome this issue, castor oil is the best option to make biodiesel because it is easier to plant and costs less than soybean, sunflower or other seeds. Castor oil is a triglyceride of various fatty acids and about 10% glycerine. The fatty acids consist of approximately 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid and 1–5% saturated fatty acids (Pazir and Muhammad, 1991).



The production processes for biodiesel are well known. There are three basic routes to biodiesel production from oils and fats that is: (a) Base catalyzed transesterification of the oil, (b) Direct acid catalyzed transesterification of the oil, and (c) Conversion of the oil to its fatty acids and then to biodiesel. Most of the biodiesel produced today is done with the base catalyzed reaction because it is low temperature and pressure; it yields high conversion (98%) with minimal side reactions and reaction time (Anonymous, 2007).

Different studies have been carried out using different alcohol. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however methanol is the most commonly used alcohol because of its low cost and its physical and chemical advantages associated with being polar and the shortest chain alcohol. The reaction time is shorter in the methanolysis because of the physical and chemical properties of methanol. The production of castor oil was faster with methanol compared with ethanol (Meneghetti, 2006).

The conventional production of biodiesel proceeds in transesterification of oils or fats using homogeneous catalysts but it will cause production of wastewater from washing process of catalyst residues and unreusability of the catalysts (Macleod et. al., 2008). Therefore, the development of heterogeneous solid catalyst has recently gained much attention on view of separation and does not produce soap through free fatty acid neutralization and triglyceride saponification. Generally,  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Ca}(\text{OH})_2$  is the raw material to produce  $\text{CaO}$ . There are several natural calcium sources from wastes such as egg shell, mollusk shell, and bone. Solid catalyst is not dissolved in the reaction and it can easily separate from products. The catalyst can be regenerated and reused and it is environmental friendly.

This research is about the production of biodiesel from castor oil using egg shell waste as solid catalyst in batch system.

## **1.2 PROBLEM STATEMENT**

The world demands for diesel keep increasing year by year. We have to face the fact that the world going to run out of oil eventually. Diesel from fossil oil are limited and non renewable. Feasibility of raw material for diesel product is looking forward. Therefore, this research will be focus on the optimum parameter and catalyst to improved yield and quality of biodiesel fuel.

## **1.3 RESEARCH OBJECTIVES**

The objective of this experiment is to produce biodiesel from castor oil using activated egg shell waste as solid catalysts and to investigate the effect of methanol/oil ratio, temperature and reaction time on the biodiesel yield

## **1.4 SCOPES OF STUDY**

In order to achieve the objective of this research, the scope of study has been determined:

1. Preparation of activated egg shell as solid catalyst.
2. Transesterification of castor oil with activated egg shell to produce biodiesel.
3. Investigation the temperature, reaction time, methanol/oil ratio effect on the biodiesel yield
4. Analyze the biodiesel yield using Gas Chromatography and ASTM standards.

## **1.5 SIGNIFICANCE OF STUDY**

Petroleum content in the world today is significantly reduced and need an alternative fuel to cover the market demand. Therefore, biodiesel production has been seen as an alternative fuel. For production of biodiesel, the choice of feedstock depends largely on the resources availability. The most assessed vegetable oils in the transesterification reaction are the castor, corn, cottonseed, crambe, peanut, soybean, palm, rapeseed, and sunflower oils, mainly due to their content of glycerides (Demirbas, 2005). Castor bean is one of the raw materials that are available in Malaysia and the oil can be extract to produce biodiesel since castor oil is amongst the plants with the highest oil yield potential. Several heterogeneous catalyst have been employed in the biodiesel production but using egg shell as a catalyst is a new development to convert waste to wealth. Wei et al. (2009) have done their studies from soybean oil that is edible oil but due to demand for nutritional need, feedstock from non edible oil has been looking forward.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 BIODIESEL**

The history of biodiesel starts in the mid 1800's. In those days the process of transesterification was used to separate glycerine from oil. Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil. When Rudolf Diesel demonstrated his diesel engine at the Paris Show in 1900, he ran it on straight peanut oil.

Technically, biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from renewable feed stocks like vegetable oils or animal fats which conform to ASTM D6751 specifications (EN 14214 in Europe) for use in diesel engines. It is biodegradable, non-toxic, show low emission profiles and also is beneficial environmentally (Fangrui and Milford, 1999). The biodiesel fuels derived from oils or fats with significant amounts of saturated fatty compounds will display higher cloud points and pour points (Bhale et al., 2008).

Non-edible vegetable oils, such as *Pongamia pinnata* (Karanja or Honge), *Jatropha curcas* (Jatropha or Ratanjyote), *Madhuca iondica* (Mahua) and Castor Oil have also been found to be suitable for biodiesel production (Yusuf et al., 2011). There are four primary techniques for biodiesel production: direct use and blending of raw oils, micro emulsions, thermal cracking and transesterification (Siddiquee and Rohani, 2011). Alkyl esters can be produced through transesterification of triglycerides, which are separated by immiscibility and higher density (Marchetti et al., 2007).

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol (with or without catalyst) to form esters and glycerol. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side (Fangrui and Milford, 1999). Under transesterification reaction with alcohol the first step is the conversion of triglycerides to diglycerides, which is followed by the subsequent conversion of higher glycerides to lower glycerides and then to glycerol, yielding one methyl ester molecule from each glyceride at each step (Hideki et al., 2001).

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages (Mustafa, 2011). It is an alternatives fuel for diesel engines that is produced by chemical reaction of a vegetable oils or animal fats with an alcohol such as methanol. The product is called as methyl ester or biodiesel, which is receiving high attention as an alternative, nontoxic, biodegradable and renewable diesel fuels (Ma and Hanna, 1999). When biodiesel displaces petroleum diesel, it reduces global warming gas emission such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. These characteristics of biodiesel reduces the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compare petroleum-based diesel fuels (Graboski and McCormick, 1998). Therefore, biodiesel has become one of the most common bio-fuels in the world (Lin et al., 2011).

## **2.2 RAW MATERIAL**

There are several types of raw materials for biodiesel production. The most common feedstock comes from vegetable oil. There are two types of vegetable oils that are edible and non-edible oils. More than 95% of biodiesel production feedstocks come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large-scale production of biodiesel from edible

oils may bring global imbalance to the food supply and demand market (Gui et al., 2008).

## **2.2.1 Edible Oil**

### **2.2.1.1 Soybean Oil**

Soybean oil is one of the major feedstocks for biodiesel production. Soybean oil has five fatty acids: approximately equal amounts of palmitic acid, oleic acid, and linolenic acid (about 13% each), linoleic acid (approximately 55%), and stearic acid (approximately 4%) (Kinney and Clemente, 2005).

## **2.2.2 Non-Edible Oil**

### **2.2.2.1 Jatropha Oil**

Jatropha oil is produced from the seeds of jatropha that has the capacity to grow in marginal and common lands. Jatropha contain high seed yield and high oil content (Wood, 2005). Jatropha oil can be used as renewable source like biodiesel.

### **2.2.2.2 Castor Oil**

Castor oil is one of the top ten oils in the world and needs only 4 months for harvesting. Considering all the options available among non-edible vegetable oil, *riccinnus communis* has been identified as the most suitable seed. Castor oil (*riccinnus communis*) is the best source for creating biodiesel (Anonymous, 2001). Castor oil and its derivatives, besides being used in medicine, are used in a wide range of sectors including agriculture, textile industry, paper industry, high quality lubricants, plastics engineering, rubber and pharmaceuticals (Ogunniyi, 2006). Consequently, there has been a steady increase in the demand of castor oil and its products in the world market due to their renewable nature, biodegradability and eco-friendliness. The use of castor oil as biodiesel has proven to have technical and ecological benefits and provides opportunities for agricultural development in marginal and sub-marginal lands.

## 2.3 CATALYST

A substance that speeds up a chemical reaction, but is not consumed by the reaction; hence the catalyst can be recovered unchanged at the end of the reaction. Excess amount of catalyst would lead to the higher amount of production cost and reduce product yield (Ma and Hanna, 1999). Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst.

### 2.3.1 Homogeneous Catalyst

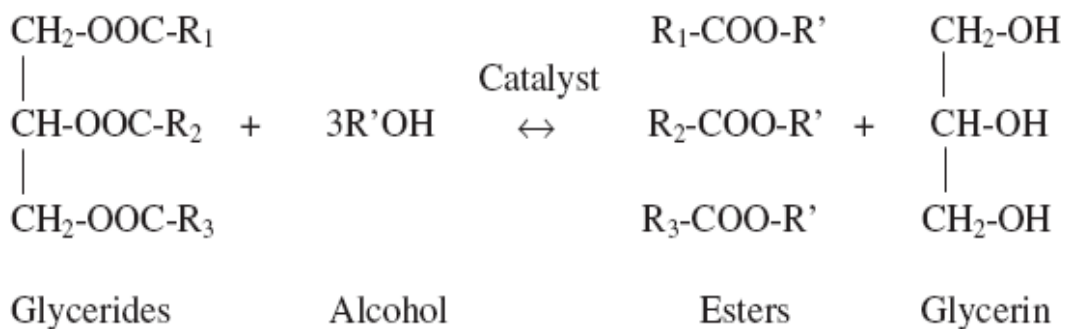
Homogeneous catalysts function in the same phase (liquid, gaseous, etc.) as the reactants. Homogeneous catalysts are dissolved in a solvent with the substrates. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) and alkali catalyst ( $\text{KOH}$  or  $\text{NaOH}$ ). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du *et al.*, 2004).

### 2.3.2 Heterogeneous Catalyst

Heterogeneous catalysis occurs in a different phase than the reactants. Heterogeneous catalysts are more economical and ecologically friendly. Heterogeneous catalysts are also easier to separate from liquid products and can be designed to give higher activity, selectivity and longer lifetimes (Tanabe and Holderich, 1999). Because of these advantages, research on chemical reaction using solid bases as catalysts has increased over the past decade. The use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification. The most commonly studies for heterogeneous basic catalysts are alkaline metals carbonates ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ), alkaline earth metal carbonates ( $\text{CaCO}_3$ ), alkaline earth metal oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ) and other oxides as  $\text{ZnO}$  (Verziu *et al.*, 2008).

## 2.4 TRANSESTERIFICATION PROCESS

In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction.



**Figure 2.1:** Reaction for oil transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as in the following equation. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. Alkaline-catalyzed transesterifications proceed considerably faster than acid-catalyzed transesterifications (Freedman et al., 1984).



## **CHAPTER 3**

### **METHODOLOGY**

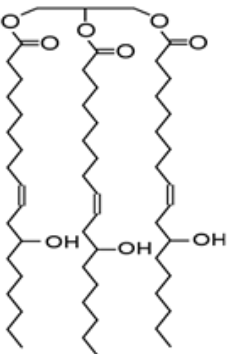
There will be an explanation about the material used and detailed procedure that be going through in the experiment to achieve the objective of this research.

#### **3.1 MATERIALS**

##### **3.1.1 Chemical**

###### **3.1.1.1 Castor Oil**

The raw material that is castor oil was bought from Sigma-Aldrich. The structure of the major component of castor oil are Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feed stocks.

Average composition of Castor seed oil / <a href="#">fatty acid</a> chains				Structure of the major component of castor oil
Acid name	Average Percentage Range			
<a href="#">Ricinoleic acid</a>	85	to	95%	
<a href="#">Oleic acid</a>	6	to	2%	
<a href="#">Linoleic acid</a>	5	to	1%	
<a href="#">Linolenic acid</a>	1	to	0.5%	
<a href="#">Stearic acid</a>	1	to	0.5%	
<a href="#">Palmitic acid</a>	1	to	0.5%	
<a href="#">Dihydroxystearic acid</a>	0.5	to	0.3%	
Others	0.5	to	0.2%	

**Figure 3.1:** Average composition of fatty acid chain and structure of the major component of castor oil.

Source: <http://casakinabalu.com>,2012

**Table 3.1:** Properties of Castor oil

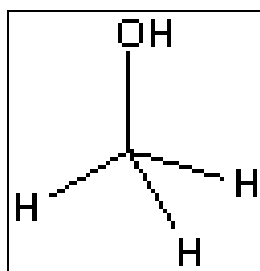
Colour	Faillty Yellow
Relative Density at 20°C	0.952-0.965
Moisture	0.3% max.
Iodine Value	82-90
Acid Value	2.0 max.
Peroxide Value	5.0 max.

### 3.1.1.2 Solid Catalyst

Solid catalyst used in this research is made from waste egg shell. We explored the possibility of application of egg shell as a catalyst in catalytic process in biodiesel production. The chemical composition (by weight) of eggshell has been reported as follows: Calcium carbonate (94%), Magnesium carbonate (1%), Calcium phosphate (1 %), and Organic matter (4%) (Stadelman, 2000).

### 3.1.1.3 Methanol

Methanol is the simplest alcohol also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits. It is light, volatile, colorless, flammable chemical with formula  $\text{CH}_3\text{OH}$  (often abbreviated  $\text{MeOH}$ ). At room temperature it is a polar liquid. Boiling point for methanol is at  $64.96^\circ\text{C}$  ( $148.93^\circ\text{F}$ ) and solidifies at  $-93.9^\circ\text{C}$  ( $-137^\circ\text{F}$ ).



**Figure 3.2:** Formula structure of methanol

### 3.1.2 Apparatus

The list of major apparatus that used in this research

- i. Two neck round bottom flask, 1000 mL
- ii. Reflux condenser
- iii. Separator funnel
- iv. Thermometer
- v. Beaker
- vi. Retort stand

### 3.1.3 Equipments

The list of major equipment used in this research

- i. Weight balance
- ii. Magnetic stirrer with hot plate
- iii. Rotary evaporator
- iv. Gas chromatography

### 3.1.3.1 Rotary Evaporator Working Principle

Rotary evaporator is used to evaporate solvents under vacuum condition with the use of heat and rotation. The rotation of the evaporation flask is to distribute the surface into bigger surface to increase the evaporation process. As the flask is rotating, heat is applied by immersing the flask in a water bath. Rotation leads to more efficient temperature transfer. The function of vacuum is to lower the boiling temperature thus minimizing damage to thermolabile substances.

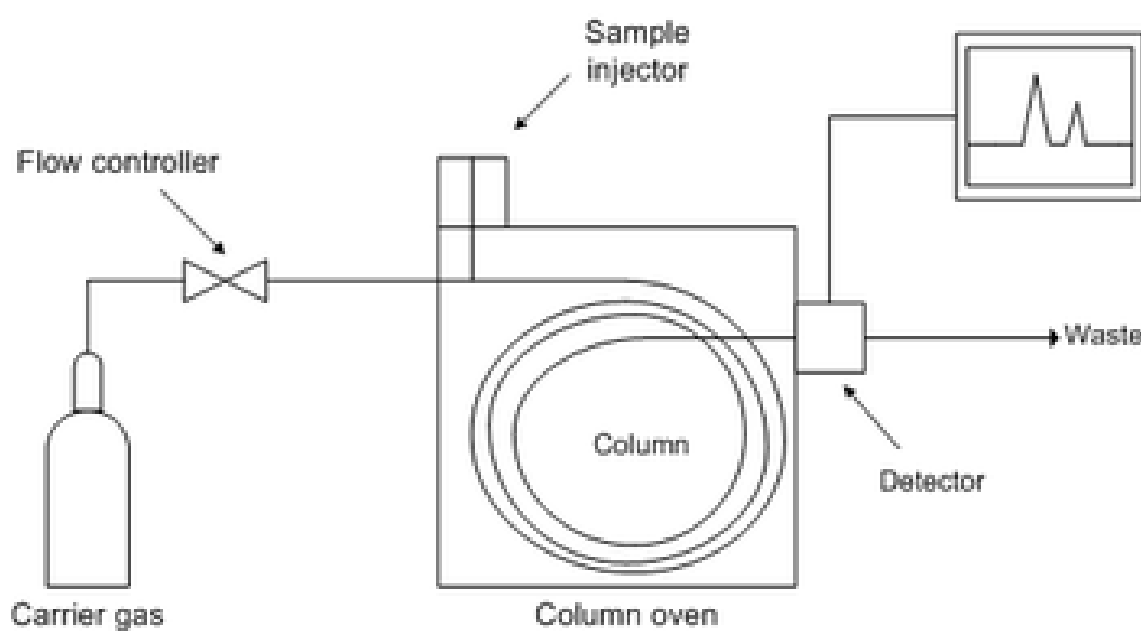


**Figure 3.3:** Rotary Evaporator

### 3.1.3.2 Gas Chromatography Working Principle

Gas chromatograph (GC) is one of the common types of chromatography in analytical chemistry for separating and analysis. Figure 3.4 show gas chromatography principle. Usually GC is used to detect the compound that can be vaporized without decomposition. The mobile phase is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen.

In all chromatographic separations the sample is transported in a mobile phase, which may be a gas, a liquid, or a supercritical fluid. This mobile phase is then forced through an immiscible stationary phase, which is fixed in place in a column or on a solid surface. The two phases are chosen so that the components of the sample distribute themselves between the mobile and stationary phase to varying degrees.



**Figure 3.4:** Gas chromatography principle

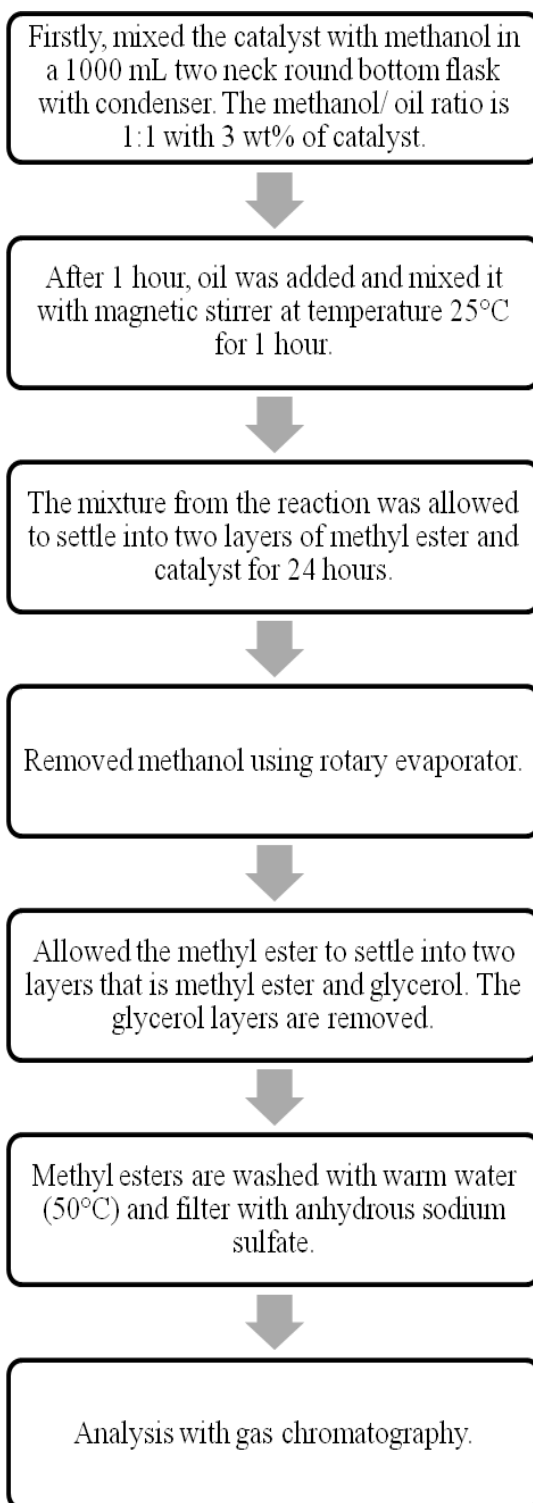
## **3.2 Methodology**

### **3.2.1 Catalyst Preparation**

Egg shell was collected from Sungai Wang Cake Shop, Jalan Haji Abdul Aziz, Kuantan. In order to remove the impurity, the egg shell was rinsed with deionized water. Then egg shell was dried for 24 hour in dry oven at 100 °C. The dried egg shell is blended into small particle. Calcination process was performed in the muffle furnace at 1000 °C for 2 hours under static air.

### **3.2.2 Transterification Procedure**

The reaction was carried out in a 1000-mL two neck round bottom flask equipped with a condenser, thermometer and a magnetic stirrer. 3 wt % (catalyst/oil weight ratio) of catalyst was added with required volume of methanol (99.5%, commercial grade) and heated to a controlled temperature of 60°C by a water bath for 1 hour. 50 g oil was added with the mixture and the reaction mixture was stirred for 1 hour. The mixture was allowed to settle for 24 hours in the separator funnel to allow catalyst to separate from methyl ester which is denser at the bottom. Then methanol was removed from the methyl ester using a rotary evaporator. The methyl ester is then put into separator funnel and two layers of methyl ester and glycerol were appeared. The glycerol are remove and methyl esters are washed with warm water (50°C) to remove residual methanol and glycerol. It was then dried (remove moisture) with anhydrous sodium sulfate and filtered before characterization.



**Figure 3.5:** Flow diagram of biodiesel production from castor oil

### **3.2.3 Experimental Studies on the Effect of Difference Operating Parameters**

Yield of biodiesel was affected by reaction variable which are methanol/oil ratio, reaction time and temperature. The methanol/oil ratio used was varied from 1:1-9:1. For reaction time, the reaction was varies from 1-5 hours while temperature are varies from 25-65°C.

The reaction process was determined by constant the reaction time at 1 hour and temperature at 25°C while methanol/oil ratio were manipulate variable. The highest yield obtained from the first manipulate variable were applied into next parameter as constant variable and manipulate the next parameter.

### **3.2.4 Analysis Procedure**

For the identification of FAME, an analysis by Gas chromatography was done for the sample of biodiesel from castor oil.

#### **3.2.4.1 GC analysis procedure for 1% sample**

- i. 10µL sample are taken using micropipette.
- ii. 990µL solvent (hexane with purity of 99.9% GC grade, analytical grade, HPLC @ GC grade).
- iii. Both sample and solvent are mixed.
- iv. Filtered using 0.2µm using syringe filter.
- v. After that, the solution is transferred into vial.
- vi. GC-MS analysis.



**Table 3.2:** GC-MS parameters for FAME analysis

<b>GAS CHROMATOGRAPH</b>	<b>FAME Analysis</b>
Injector temperature	200°C
Column Flow	1 ml/min
Split flow	30 ml/min
Injection volume	1ul
<b>Oven Temperature</b>	
Initial temperature	70°C
Hold temperature	3 mins
Ramp	7°C/min
Final Temperature	230°C
Hold time	3 mins

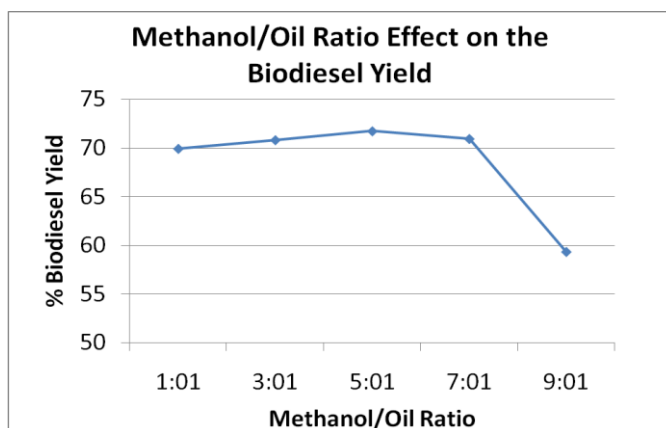
## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 BIODIESEL PRODUCTION

##### 4.1.1 Effect of Methanol/Oil Ratio

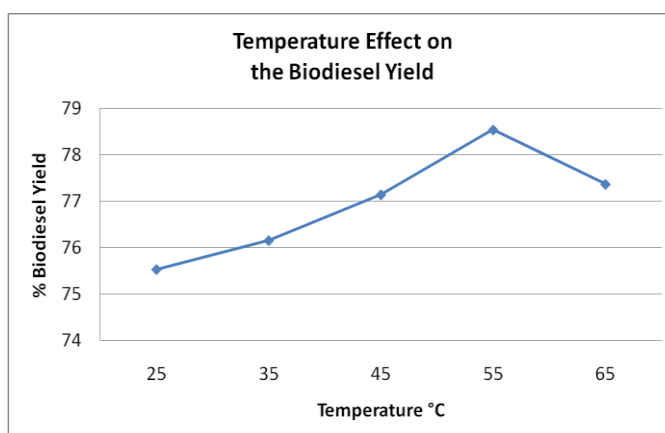
The methanol/ oil ratio effect on biodiesel production using solid catalyst shows that the yield of the biodiesel production increased up to 72 % at 5:1 of methanol/oil ratio. Transesterification activity depends on the molar concentration of methanol/oil ratio. Large excess of methanol is required to shift the equilibrium favorably during transesterification for better yields of biodiesel (Sree et al., 2009). The graph shows experimental condition where methanol/oil ratio increase from 1:1 to 5:1 while slight decrease of % biodiesel yield from 5:1 to 7:1. With higher molar oil ratio, production is increased but the recovery of biodiesel is decrease due to poor separation of glycerol (Balat, 2010).



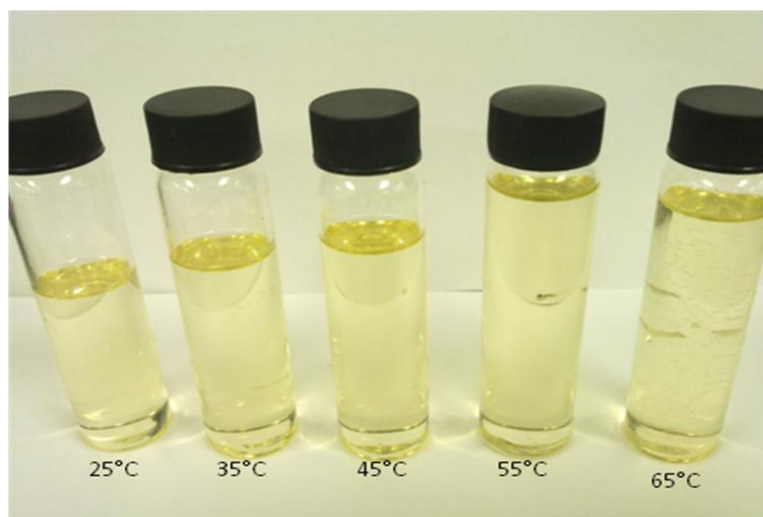
**Figure 4.1:** The effect of methanol/oil ratio on the biodiesel yield

#### 4.1.2 Effect of Temperature

The effect of reaction temperature on the % biodiesel yield was studied with five temperatures; 25°C, 35°C, 45°C, 55°C and 65°C. The result shows that transesterification proceeded slowly at 25°C where the conversion was 75.5%. The lower temperature resulted in lower conversion because only small amount of molecules was able to get over the required energy barrier (Zeng et al., 2008). The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization (Leung et al., 2010). The % biodiesel yield increase up to 78.5% at 55°C and decreasing at 65°C which near to the boiling point of methanol. This probably because the molar rate of methanol to oil decreased when methanol reactant volatilized into gas phase above the boiling point of methanol. The experimental result shows the % biodiesel yield of biodiesel production increasing to 55°C and decreasing at 65°C. This shows that the highest biodiesel yield obtained at temperature 55°C.



**Figure 4.2:** The effect of temperature on the biodiesel yield

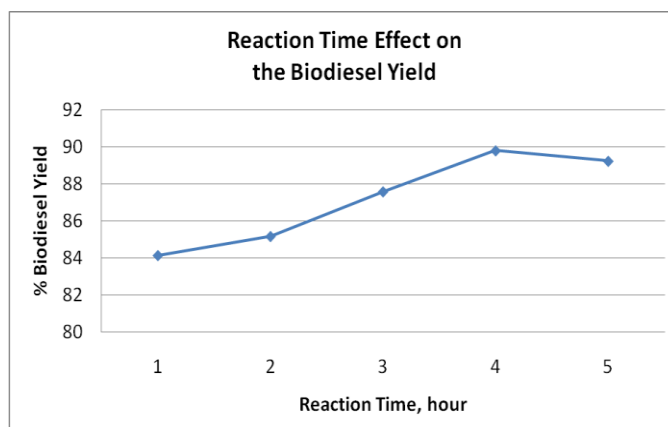


**Figure 4.3:** Biodiesel sample for reaction temperature

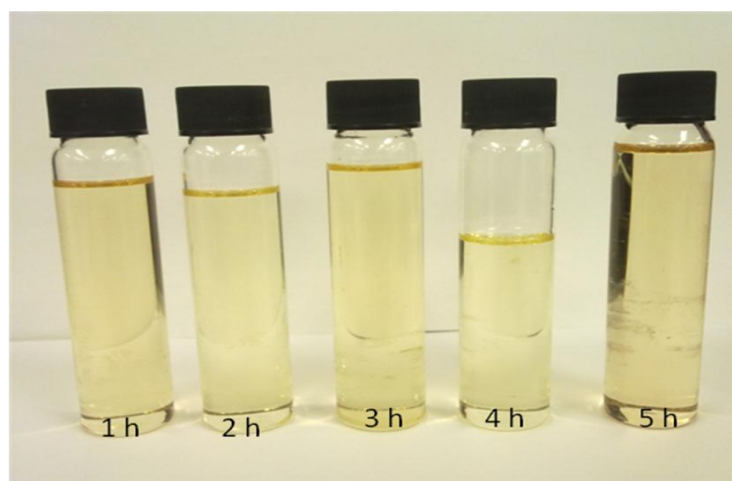
From the observation, sample at 65°C are less viscous compare to sample at 25°C. Higher reaction temperature decreases the viscosities of the oils (Eevera et al, 2009).

#### **4.1.3 Effect of Reaction Time**

The effect of reaction time on the % biodiesel yield was studied with five reaction time; 1, 2, 3, 4 and 5 hours. The experimental result shows the % biodiesel yield of biodiesel production increasing to maximum conversion of 89.8 % was obtained at 4 hours reaction time. Reaction at 5 hours indicate that excess reaction time will lead to a reduction in product yield. This is because no significant effect on the conversion of triglycerides due to backward reaction of transesterification resulting in loss of esters (Eevera et al, 2009).



**Figure 4.4:** The effect of reaction time on the biodiesel yield



**Figure 4.5:** Biodiesel sample for reaction time

From the observation, the colour for the sample at 5 hour reaction time change into dark yellow compare to other reaction time sample. This is probably caused by the high temperature and long reaction time that could burn some of the oil (Miao et al., 2006).

## 4.2 BIODIESEL PROPERTIES

**Table 4.1:** Properties of Methyl Esters of Castor Oil

Properties	ASTM Protocol	Limit	Castor Oil (This work)	Bello E.I and Makanju.A., 2004
Specific Gravity	-	-	0.8523	0.8643
Calorific value (mJ/kg)	D240	-	37	32
Acid Value (mg KOH/g)	-	0.50 mg KOH/g (max)	0.03	0.01

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 CONCLUSION**

- Biodiesel has been successfully produced from castor oil using activated egg shell waste as solid catalyst.
- The variation of methanol/ oil ratio, temperature and reaction time has affected the biodiesel yield.
- The highest biodiesel yield was found by the methanol/ oil ratio of 5:1, temperature of 55°C and reaction time of 4 hours.

#### **5.2 RECOMMENDATIONS**

- Further investigation on difference condition for activation of catalyst.
- Analyze the solid catalyst sample to check the component.
- Search the relationship between methanol/oil ratio and other parameters and it optimal condition.

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## **APPENDIX**

## APPENDIX A

### Picture of Calcinations Process



**Figure A-1:** Egg shell was rinsed with deionized water



**Figure A-2:** Blending process



**Figure A-3:** Calcinations process



**Figure A-4:** Solid catalyst

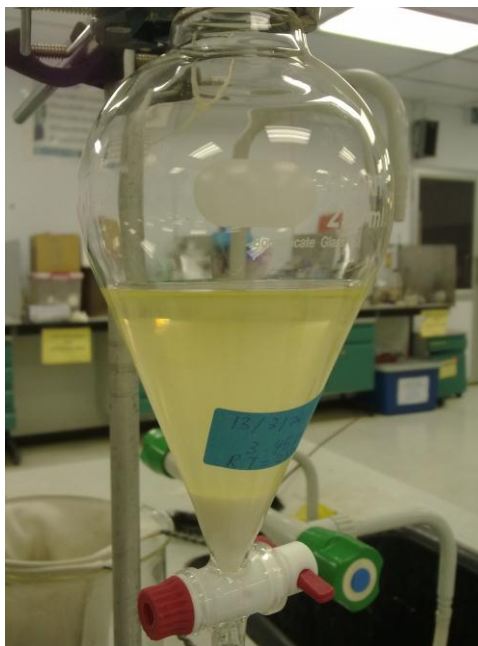
### Picture of Transesterification Process



**Figure A-5:** Batch system reactor for reaction process



**Figure A-6:** Catalyst activation process



**Figure A-7:** Separation process



**Figure A-8:** Methanol recovery process





**Figure A-9:** Washing process



**Figure A-10:** Filtration process

## APPENDIX B

### Table of Variable Parameter

**Table B-1:** Variable parameter for methanol/oil ratio

Methanol/oil ratio	Temperature (°C)	Reaction Time (h)
1:1	25	1
3:1	25	1
5:1	25	1
7:1	25	1
9:1	25	1

**Table B-2:** Variable parameter for temperature

Temperature (°C)	Methanol/oil ratio	Reaction Time (h)
25	5:1	1
35	5:1	1
45	5:1	1
55	5:1	1
65	5:1	1

**Table B-3:** Variable parameter for reaction time

Reaction Time (h)	Methanol/oil ratio	Temperature (°C)
1	5:1	55
2	5:1	55
3	5:1	55
4	5:1	55
5	5:1	55

## APPENDIX C

### Gas Chromatography Result

**Table C-1:** Methanol Oil Ratio Effect on % Biodiesel Yield

<b>Methanol/Oil</b>	<b>1: 1</b>	<b>3: 1</b>	<b>5: 1</b>	<b>7: 1</b>	<b>9: 1</b>
Weight	35.679	35.407	35.911	35.469	29.673
% Area	97.99	100	99.87	100	99.98
% Biodiesel Yield	69.92	70.81	71.73	70.94	59.33

**Table C-2:** Temperature Effect on % Biodiesel Yield

<b>Temperature</b>	<b>25</b>	<b>35</b>	<b>45</b>	<b>55</b>	<b>65</b>
Weight	37.907	38.447	38.914	39.27	38.777
% Area	99.63	99.04	99.12	100	99.76
% Biodiesel Yield	75.53	76.16	77.14	78.54	77.37

**Table C-3:** Reaction Time Effect on % Biodiesel Yield

<b>Reaction time</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Weight	42.07	42.589	43.89	44.988	44.983
% Area	100	99.99	99.78	99.81	99.19
% Biodiesel Yield	84.14	85.17	87.59	89.81	89.24